REPORT DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
02-09-2014	Final	5 March 2013 – 4 March 2014

4. TITLE AND SUBTITLE

Steric Control of Complex Chemical Reactions

5a. CONTRACT NUMBER

FA2386-13-1-4027

5b. GRANT NUMBER

Grant AOARD-134027

5c. PROGRAM ELEMENT NUMBER

61102F

6. AUTHOR(S)

Dr. Kopin Liu

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Institute of Atomic and Molecular Sciences
PO Box 23-166 Academia Sinica
Taipei 10617
Taiwan

8. PERFORMING ORGANIZATION REPORT NUMBER

N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AOARD
UNIT 45002
APO AP 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/AFOSR/IOA(AOARD)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

AOARD-134027

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution A: Approved for public release. Distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The aim of this project, together with 2 previous 1-year grants sought to understand and ultimately to stereo-control the reactive outcome of polyatomic reactions by vibrational excitations of reactants. Specifically, we unraveled the steric effects of chemical reactions with two complementary experimental approaches: (1) by selecting a single ro-vibrational state of reactants, and (2) by pre-aligning the reactive bonds in space.

15. SUBJECT TERMS

Molecular Dynamics, Molecular Beam Experiments, Reaction Mechanisms

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Ingrid J. Wysong, Ph.D.
U	U	U	SAR	8	19b. TELEPHONE NUMBER *(Include area code)* +81-42-511-2000

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
03 SEP 2014	**Final**	**05-03-2013 to 04-03-2014**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Steric Control of Complex Chemical Reactions	**FA2386-13-1-4027**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER **61102F**
6. AUTHOR(S) **Kopin Liu**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Institute of Atomic and Molecular Sciences,PO Box 23-166 Academia Sinica,Taipei 10617,Taiwan,NA,NA**	8. PERFORMING ORGANIZATION REPORT NUMBER **N/A**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **AOARD, UNIT 45002, APO, AP, 96338-5002**	10. SPONSOR/MONITOR'S ACRONYM(S) **AFRL/AFOSR/IOA(AOARD)**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) **AOARD-134027**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The aim of this project, together with 2 previous 1-year grants sought to understand and ultimately to stereo-control the reactive outcome of polyatomic reactions by vibrational excitations of reactants. Specifically, we unraveled the steric effects of chemical reactions with two complementary experimental approaches: (1) by selecting a single ro-vibrational state of reactants, and (2) by pre-aligning the reactive bonds in space.

15. SUBJECT TERMS
Molecular Dynamics, Molecular Beam Experiments, Reaction Mechanisms

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**8**	

(1) Cover page

Final Technical Report

Title: Steric Control of Complex Chemical Reactions

Principal Investigator(s): Kopin Liu

Contract Number: FA2386-13-1-4027

AFOSR/AOARD Reference Number: AOARD-134027

AFOSR/AOARD Program Manager: Ingrid Wysong

Period of Performance: 1 APRIL 2011 – 31 MARCH 2014

Submission Date: 31 MAY 2014

PI: Kopin Liu / Institute of Atomic and Molecular Sciences

(2) Objectives

The aim of this three-year proposal is to understand and ultimately to stereo-control the reactive outcome of polyatomic reactions by vibrational excitations of reactants. Specifically, we unraveled the steric effects of chemical reactions with two complementary experimental approaches: (1) by selecting a single ro-vibrational state of reactants, and (2) by pre-aligning the reactive bonds in space.

(3) Status of the Efforts

Reactions of methane with F, Cl, and O(^{3}P) atoms are of prototypical H-atom abstraction mechanism, yet with vastly different energetic and barrier properties. As such, their contrasting behaviors upon vibrational and translational excitations can serve as benchmarks to gain deeper insights into polyatomic reaction dynamics and to address the question of how to generalize the Polanyi's rule that is formulated for atom + diatom reactions. Exploiting the product pair-correlation measurement further enables us to elucidate the energy flow in the transition-state region of a chemical reaction, and to shed new light onto the mode- and bond-selective chemistry. We envision that the mode- and bond-selectivity are intimately related to the stereo-specificity of a reaction. To this end, we explored in this proposal two complementary approaches by either selecting a single rotational state of methane reactants or pre-aligning the reactive bond axis in the collisional frame. We conjecture that the combination of these two approaches will add a new dimension to polyatomic reaction kinetics and dynamics.

The publications (item 6) and the conference lectures (item 7) listed below describe the works performed under the support of this AFOSR/AOARD grant. In addition, I have the honours to be recognized by several international awards (item 8). Needless to say, those will not be possible without the continuing supports from AFOSR/AOARD since 2008.

(4) Abstract

The crossed molecular beam experiment was performed using the rotating source machine at IAMS, which is equipped with a uniquely designed time-sliced velocity-map imaging detector capable of measuring the product pair correlation. Two types of setup were exploited in preparing the vibrationally excited polyatomic reactants. When the infrared (IR) laser was directed in the source chamber to excite the methane reactants, we probed the stereodynamics by

measuring the dependences of reactive outcomes on rotationally state-selected reactants and on translational energy. As the IR laser was sent directly to the scattering region, the combination of the capabilities of freely rotating the two molecular beams at will and the time-sliced imaging detection enables us to uniquely unravel the full three-dimensional stereodynamics of a reaction, as demonstrated in our 2012 *Nature Chemistry* paper. The detailed methodology is described in the 2014 *Journal Chemical Physics* paper (#13).

The most significant contributions during this period are the two papers published in *Science* **331**, 900-903 (2011) and *Nature Chemistry* **4**, 636-641 (2012), respectively. In the *Science* paper, we introduced the concept of "passive" and "active" stereo-controls by contrasting the results in the reactions of $CHD_3(v_1=1)$ with F, Cl, and $O(^3P)$, which highlights the crucial role of the long-range anisotropic interactions in dictating the re-orientation effects. In the *Nature Chemsitry* paper, we reported the complete three-dimensional characterization of the sterics of a benchmark polyatomic reaction by measuring the dependence of the product state-resolved angular distributions on the spatial alignment of the reactive bond in a crossed molecular beam experiment. This is for the first time that a true three-dimensional view of the steric effects has been realized experimentally for any chemical reaction in the half-century history of chemical dynamics. The results demonstrated the existence of two distinct microscopic reaction mechanisms in the reaction of $Cl + CHD_3(v_1=1) \rightarrow HCl(v=0, 1) + CD_3(0_0)$. Detailed analysis further revealed that the origin of the stereodynamics in the $HCl(v=0) + CD_3(0_0)$ product channel can be captured by a textbook line-of-centres model. In contrast, a time-delay pathway, most likely mediated by reactive resonances, appeared to be operative in forming the excited $HCl(v=1) + CD_3(0_0)$ product pair. This work received immediate attention upon publication, as highlighted by *Science Editors' Choice* under the title "*Angle of Attack*" in *Science* **337**, 779 (2012). Thanks to these ground-breaking works, I will be honoured for the 2014 Bernstein Award in the upcoming International Stereodynamics Conference.

We continue the stereodynamics investigations along the two complementary approaches. Currently, we are exploring the experiment with a laser pre-aligned $CH_4(v_3=1)$ reagent. The reaction of $Cl + CH_4$ is of great importance in atmosphere chemistry as being a primary competing process to the ozone-hole catalytic reaction of $Cl + O_3$ as well as a regulating process of the potent and the second most important greenhouse gas CH_4 in the earth atmosphere.

Unlike the $CHD_3(v_1=1)$ reaction where the IR laser polarization aligns the unique C-H bond, all four C-H bonds will be collectively excited in the antisymmetric-stretching mode of $CH_4(v_3=1)$. Preliminary results are extremely exciting, which indicate a very strong steric effect. This is quite intriguing and counter-intuitive in that apparently the four stretching-excited C-H bonds are not completely equivalent in this chemical reaction! To gain deeper insights into this intriguing phenomenon, we adopted the other approach is to investigate the effects on reactivity by initial rotational-state selection. We believe the information thus obtained will complement the above alignment measurement. Together, they may shape up our thinking and help us formulate a conceptual framework for polyatomic reactivity in general.

(5) Personnel Supported

Dr. Fengyan Wang (left for a faculty position at Fudan University, Shanghai)

Dr. Ondrej Thac

Dr. Yuan Cheng

Dr. Huilin Pan

Mr. Jui-San Lin (Ph.D. student at NTU)

Ms. Queiya Chang (research assistant)

Ms. Rui-Ting Chu (research assistant)

(6) Publications

2011

1. *Steric Control of the Reaction of CH Stretch-Excited CHD_3 with Chlorine Atom*
   F. Wang, J.-S. Lin, and K. Liu, *Science* **331**, 900-903 (2011).
2. *Imaging the Reaction Dynamics of $O(^3P) + CH_4 \rightarrow OH + CH_3$*
   J. Zhang and K. Liu, *Chemistry- an Asian J.* **6**, 3132-3136 (2011)
3. *Experimental Signatures for a Resonance-Mediated Reaction of Bend-Excited $CD_4(v_b=1)$ with Fluorine Atoms*
   F. Wang and K. Liu, *J. Phys. Chem. Lett.* **2**, 1421-1425 (2011).

2012

4. *Quantum Dynamical Resonances in Chemical Reactions: From A + BC to Polyatomic Systems*

K. Liu, *Adv. Chem. Phys.* **149**, 1-46 (2012).

5. *Translational Energy Dependence of the Cl + CH_4(v_b=0,1) Reactions: A Joint Crossed-Beam and Quasiclassical Trajectory Study*

   B. Zhang, K. Liu, G. Czako, and J. M. Bowman, *Mol. Phys.* (*D. Herschbach issue*) **110**, 1617-1626 (2012).

6. *Imaging the Effects of the Antisymmetric Stretch Excitation of CH_4 in the Reaction with F Atom*

   H. Kawamata, W. Zhang, and K. Liu, *Faraday Disc.* **157**, 89-100 (2012).

7. *Revealing the Stereospecific Chemistry in the Reaction of Cl with Aligned CHD_3(v_1=1)*

   F. Wang, K. Liu, and T. P. Rakitzis, *Nature Chem.* **4**, 636-641 (2012).

2013

8. *Vibrational Enhancement factor of the Cl + CHD_3(v_1=1) Reaction: Rotational-Probe Effects*

   F. Wang, J.-S. Lin, Y. Cheng, and K. Liu, *J. Phys. Chem. Lett.* **4**, 323-327 (2013).

9. *Imaging the Effects of Bend-Excitation in the F + CD_4(v_b=0, 1) → DF(v) + CD_3(v_2=1, 2) Reactions*

   F. Wang and K. Liu, *J. Phys. Chem. A* **117**, 8536-8544 (2013).

10. *Crossed-Beam and reduced Dimensionality Studies of the State-to-State Integral Cross Sections of the Cl + HCD_3(v) → HCl(v') + CD_3 Reaction*

    X. Shan, S. R. Remmert, D. C. Clary, B. Zhang, and K. Liu, *Chem. Phys. Lett.* **587**, 88-92 (2013).

11. *Steric Effects in the Cl + CHD_3(v_1=1) Reaction (Journal cover page)*

    F. Wang and K. Liu, *Chinese J. Chem. Phys.* **26**, 706-710 (2013).

2014

12. *On the Signal Depletion Induced by Stretching Excitation of Methane in the Reaction with F Atom*

    Y. Cheng, H. Pan, F. Wang, and K. Liu, *Phys. Chem. Chem. Phys.* **16**, 444-452 (2014).

13. *How to Measure a Complete Set of Polarization-Dependent Differential Cross Sections in a Scattering Experiment with Aligned Reagents?*

    F. Wang, J.-S. Lin, and K. Liu, *J. Chem. Phys.* **140**, 084202 (2014).

14. *Imaging the Effects of the Antisymmetric-Stretching Excitation in the O(^3P) + CH_4(v_3=1) Reaction* (*Communication*)

H. Pan and K. Liu, *J. Chem. Phys.* **140,** 191101 (2014).

(7) Interactions:

(a) Invited Talks at International Conferences

1. *"Marie Curie ICONIC Training School"*, Paris, France, June 6-11, 2011.
2. *"XXIII Conference on Dynamics of Molecular Collisions-DMC"*, Snowbird, Salt Lake City, UT, USA, July 10-15, 2011.
3. *"The 31st International Symposium on Free Radicals"*, Port Douglas, Australia, July 24-29, 2011.
4. *"Conference on Molecular Energy Transfer - COMET"*, Jesus College, Oxford, UK, Sept. 11-16, 2011.
5. *"Sustainable Energy Workshop"*, IAMS, Taipei, Taiwan, Dec. 15-16, 2011.
6. *"22nd International Symposium on Gas Kinetics"*, Boulder, Colorado, USA, June 18-22, 2012.
7. *"Molecular Reaction Dynamics in Gases, Liquids and Interfaces: FD157"*, Assisi, Italy, June 25-27, 2012.
8. *"Gordon Research Conference on Atomic and Molecular Interactions"*, Stonehill College, MA, USA, July 15-20, 2012.
9. *"5th Cross-Strait Workshop on Chemical Dynamics"*, Yellow Mountain, Anhui, China, Aug. 27-30, 2012.
10. *"International Meeting of ICONIC Marie Curie Initial Training Network"*, London, UK, Nov. 2-4, 2012
11. *"Symposium on Atomic and Molecular Sciences"*, Taipei, Taiwan, Nov. 12, 2012.
12. *"Electronic Structure and Dynamics of Molecule and Clusters – ESDMC"*, Kolkata, India, Feb. 17-20, 2013.
13. *"XXV International Symposium on Molecular Beams"*, Prague, Czech Republic, June 9-13, 2013.
14. *"XXIV Conference on Dynamics of Molecular Collisions"*, Granilibakken, CA, July 7-12, 2013.
15. *"XIII National Chemical Dynamics Symposium"*, Wuhu, China, Aug. 23-26, 2013.
16. *"NSRRC Workshop on IR-VUV Science"*, Hsinchu, Taiwan, Aug. 29-30, 2013.

17. *"12th Trombay Symposium on Radiation & Photochemsitry TSRP-2014"*, BARC, Mumbai, India, Jan. 6-9, 2014.
18. *"6th Cross-Strait Workshop on Chemical Dynamics"*, Hualian, Taiwan, Feb. 16-18, 2014.
19. *"2014-Asian Core Winter School"*, Taipei, Taiwan, Feb. 24-26, 2014.

(b) International Collaborations

Our works on the reaction dynamics of vibrationally excited (aligned or not) methane with F, Cl, and O(^{3}P) atoms have received considerable attentions in the international community. Currently we are collaborating with a number of theoretical groups worldwide on various aspects of these reactions, including Joel Bowman (Emory University), Hua Guo (University of New Mexico), David Clary (Oxford University, UK), Peter Rakitzis (University of Crete, Greece), Gabor Czako (Eötvös University, Hungary), Joaquin Espinosa-Garcia (Universidad Extremadura, Spain), Miguel Gonzalez (Universidad de La Rioja, Spain), Minghui Yang (Wuhan Institute of Physics and Mathematics, China), and Dunyou Wang (Shandong Normal University, China).

(8) Honors/Awards

Richard B. Bernstein Award, XV International Stereodynamics Conference, 2014.
AS Investigator Award, Academia Sinica, 2014-2018.
Professor C. T. Chang Memorial Lectureship Award, 2014.
Honorary Lectureship, XXV International Symposium on Molecular Beams, 2013.
Fellow, Royal Society of Chemistry (UK), 2013.
CUSO (Conférence Universitaire de Suisse Occidentale) Lectureship, Switzerland, 2012.
Humboldt Research Award, Alexander von Humboldt Foundation, 2011.